

A Study of Lead Perchlorate and Its Use in Analytical Separations

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

By
James Lyle Kassner
1926

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JAMES L. KASSNER



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PART I

PREPARATIONS

Introduction

Lead perchlorate was first prepared by Serullas¹ by heating lead oxide with perchloric acid. It was also prepared by Marignac² and Roscoe³ by adding lead carbonate to perchloric acid and evaporating to a sirupy liquid. Roscoe was the first to point out the fact that lead perchlorate is extremely deliquescent. The formula of the salt which he obtained was $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$. There is no record of any other hydrate of lead perchlorate, although Hoffmann⁴ interpreted Roscoe's figures as corresponding to the formula, $\text{Pb}(\text{ClO}_4)_2 \cdot 1.5\text{H}_2\text{O}$.

Two forms of basic lead perchlorate have been described by Marignac,² Weinland⁵ and Weinland and Stroh.⁶ Marignac prepared the basic salts by boiling a concentrated solution of normal perchlorate with a slight excess of lead carbonate and evaporating the filtrate. The formula of his salt was $\text{PbO} \cdot \text{Pb}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$. Rammelsberg⁷ also prepared this same salt. Weinland^{5,6} prepared basic lead perchlorates to which he ascribed the formulas, $\text{Pb}_2(\text{ClO}_4)_2(\text{OH})_2 \cdot 1.5\text{H}_2\text{O}$ and $\text{Pb}_3(\text{OH})_4(\text{ClO}_4)_2$. He prepared the first by treating lead oxide with more than one and less than two equivalents of perchloric acid. The latter was prepared by treating three moles of lead oxide with two moles of perchloric acid and crystallized in two forms as described by Marignac.²

Experimental

Preparation of Normal Lead Perchlorate.—Lead perchlorate was prepared by adding to lead nitrate about 1% excess over the calculated amount of perchloric acid and evaporating to remove all nitric acid. Lead nitrate of c. p. grade was twice recrystallized with centrifugal drainage and washing. Perchloric acid (72%) of a high degree of purity was further purified by fractional distillation in a vacuum. It was diluted with a little water, added to the lead nitrate and the solution evaporated until fumes of perchloric acid were given off. The lead nitrate did not entirely dissolve in the acid at first but gradually went into solution as the evaporation progressed. The solution was

¹ Serullas, *Ann. chim. phys.*, **46**, 297 (1831).

² Marignac, "Oeuvres Complètes," Vol. I. p. 401 (1840-60); *Compt. rend.*, **42**, 288 (1856); *Mem. Soc. Phys. Genève*, **14**, 260 (1855); *Arch. Phys. Nat.*, **31**, 170 (1856).

³ Roscoe, *Proc. Roy. Soc. (London)*, **11**, 493 (1861); *Ann.*, **121**, 346 (1862); *J. Chem. Soc.*, **16**, 82 (1863).

⁴ Hoffmann, "Lexicon der anorg. Verbindungen," **1915**, Vol. I, p. 699.

⁵ Weinland, *Z. angew. Chem.*, **34**, 354 (1921).

⁶ Weinland and Stroh, *Ber.*, **55**, 2706 (1922).

⁷ Rammelsberg, *Handb. kryst. phys. Chem.*, **1**, 318 (1881).

tested for nitrate from time to time by adding a drop of it to a solution of diphenylamine in coned. sulfuric acid, and the fuming was continued until no test for nitrate was obtained.

Removal of Excess Perchloric Acid.—Owing to the great solubility of the salt, it was found impossible to remove the excess of perchloric acid even by two recrystallizations. It could not be volatilized by heating because anhydrous lead perchlorate, stable up to 200°, begins to decompose above that temperature into lead chloride and lead oxide, evolving both oxygen and chlorine, and also because the last traces of acid, becoming anhydrous, readily decompose into chlorine and oxygen, contaminating the salt with chloride. Moreover, the salt containing excess of perchloric acid was decomposed slightly when dehydrated in a vacuum in the presence of phosphorus pentoxide.

The obvious method of neutralizing the excess of acid by the addition of lead oxide or carbonate is not readily applicable in this case, because these substances are readily soluble in a solution of lead perchlorate, forming soluble basic salts and there is no way of knowing when just the proper amount has been added except by making rather troublesome analyses of the solution.

Because perchloric acid dihydrate, unlike the anhydrous acid, is very stable, it seemed probable that the excess of acid could be removed by passing a stream of moist air over the fused salt, as was done by Richards and Willard⁸ with lithium perchlorate. This was found to be satisfactory and because it is the most effective method for many perchlorates, it will be described in some detail.

A heater was constructed from a 20 × 30 cm. beaker which was wrapped with damp sheet asbestos and wound with seventy turns of chromel ribbon, 0.2 × 1.6 mm. The heating unit for the bottom of the beaker was made by coiling together chromel ribbon and a strip of asbestos 1 cm. wide to form a disk of suitable size which, while damp, was pressed against the bottom of the beaker. The two heating units could be connected either in series or in parallel. The beaker was insulated by asbestos wool, held in place by sheet asbestos, and the whole supported on a base of asbestos board. The beaker was covered with a quartz plate. Air purified by passing it through a solution of silver nitrate and a soda-lime tower was passed through water at about 100° by bubbling it through a three-necked Woulff bottle, electrically heated by a winding of No. 28 chromel wire, and supplied with water from a large stock bottle. The moist air passed through a delivery tube extending to within 5 cm. of the bottom of the large beaker.

The lead perchlorate solution, free from nitrate, was evaporated below 125° until it contained only a little more water than was required to form the trihydrate. This solution was then placed in the heater described above, on a support 10 cm. high, and steamed for three hours at about 160°. At the end of this time the salt was free from acid and a nephelometric test⁹ showed that it contained only a few thousandths of one per cent. of chloride.

If more than 1% excess of acid is used in preparing lead perchlorate, longer steaming will be necessary. The vapor pressure of water in the air passing through the heater must be high enough to prevent complete dehydration of the salt; otherwise considerable chloride will be formed.

In order to determine accurately the amount of free acid, a sample of 3 to 4 g. of the salt was dissolved in about 7 cc. of water free from carbon dioxide. The lead was precipitated as sulfate by the addition of excess of neutral sodium sulfate, and removed by filtration. The acid in the filtrate was determined colorimetrically by using brom thymol blue as indicator and 0.001 *N* hydrochloric acid and sodium hydroxide as standard solutions.

⁸ Richards and Willard, *J. Am. Chem. Soc.*, **32**, 4 (1910).

⁹ Richards and Wells, *Am. Chem. J.*, **31**, 235 (1904).

Crystallization of Lead Perchlorate.—Lead perchlorate is extremely soluble in water and the trihydrate melts at 83–84°. In order to obtain a satisfactory yield of crystals the amount of water present must be carefully regulated. It was found best to start with a known weight of lead nitrate and for every 500 g. of lead perchlorate trihydrate, to allow 8 to 10 g. excess of water. A semi-fluid mass was then obtained on cooling to 0°. The crystals were drained centrifugally in platinum cups and a yield of 58% was obtained. The trace of chloride originally present could not be detected nephelometrically after crystallization. The yield decreased rapidly as the amount of water increased beyond that required to form the trihydrate. For example, in the above case, 555 g. of the salt was present, and if 25 g. of water instead of 10 g. was present, no crystals appeared on cooling to 0°.

Preparation of Anhydrous Lead Perchlorate.—Lead perchlorate trihydrate, dried at room temperature with phosphorus pentoxide in a vacuum for nine months, was not completely dehydrated. To increase the rate of dehydration by drying in a vacuum at a higher temperature the following apparatus was devised. A flanged pyrex cylinder¹⁰ 60 cm. long by 12.5 cm. inside diameter and 0.5 cm. thick, was provided with covers to which were fused glass stopcocks. The flanges and covers were so carefully ground that, using only a trace of grease, the cylinder maintained a vacuum. This cylinder was placed in an electric oven 25 × 30 × 28 cm., made of "transite" asbestos board. The oven was wired in two units, the sides and bottom with twenty turns of No. 28 chromel wire and the top with twenty-two turns. There was a mica window on top and another on one side. The advantage of this apparatus was that the central portion of the cylinder, containing the salt to be dehydrated, could be heated to the desired temperature, while the ends, containing the desiccant, phosphorus pentoxide, were relatively cool.

Because anhydrous lead perchlorate takes up moisture with such extraordinary rapidity, it was necessary to handle it only in very dry air. A large tight box was constructed of wood with a plate glass top and large enough to manipulate three ordinary desiccators. It was provided with a door, made air tight by means of a soft rubber gasket. There were two "manipulating arm-holes" in which long-sleeved rubber gloves were fastened air tight. A sulfuric acid manometer was provided for observing the pressure. Air, dried successively by calcium chloride and phosphorus pentoxide, was passed into the box for a few hours before and during use.

Lead perchlorate trihydrate was placed in an evaporating dish supported in the center of the cylindrical pyrex desiccator described above. Phosphorus pentoxide placed in the cool ends of the cylinder served to remove the moisture. The oven was adjusted to maintain a temperature of 65°. It was evacuated to a pressure of 35 mm. and the drying continued for nineteen hours. The salt was then removed and weighed on a platform balance in the manipulating box. When the hydrated salt had lost about one-third of its water of hydration, the temperature was raised to 100° for eight hours and then to 120° for fourteen hours. Analysis of the salt at this time showed 50.73% of lead compared with a theoretical value of 51.02% for the anhydrous salt. The heating was continued at 120° for twenty-four hours and at the end of this time the salt contained 51.02% lead.

Analysis of Anhydrous Lead Perchlorate.—While still hot, the salt was removed from the vacuum desiccator and placed in an ordinary desiccator containing phosphorus pentoxide. This was then placed in the manipulating box along with a similar desiccator containing two tared weighing bottles with carefully ground stoppers. After flushing out the box with dry air, a sample was transferred to the weighing bottle, and replaced in the desiccator. The stoppers were so well ground that there was no gain in weight during the process of weighing.

¹⁰ Specially made by the Corning Glass Works.

The amount of lead in the salt was determined by precipitating it as lead sulfate and weighing on a Gooch crucible. Duplicate analyses gave 51.016 and 51.020% of lead as compared to a theoretical value of 51.02%.

Anhydrous lead perchlorate is white and when exposed to air takes up moisture with amazing rapidity, forming the monohydrate and trihydrate. It is stable at 200° but begins to decompose at about 250° into lead chloride and lead oxide, evolving both oxygen and chlorine. It fuses at 270–275°, and above this completely decomposes.

Preparation of Lead Perchlorate Monohydrate.—Lead perchlorate trihydrate was partially dried at room temperature in a vacuum desiccator with phosphorus pentoxide. It then contained a little more water than corresponded to the monohydrate (6.77% instead of 4.25%, calculated from a determination of lead). The pentoxide was then replaced by a large excess of anhydrous lead perchlorate and the desiccator evacuated. The salt was allowed to remain in this desiccator for fifteen months and then analyzed for lead and perchlorate.

To obtain samples without exposure to atmospheric moisture, the manipulating box was used as before. Lead was determined as sulfate and the perchlorate by precipitation with "nitron" as described by Storm¹¹ and also by removing the lead electrolytically and then titrating the acid with standard alkali using methyl red as indicator. The results were as follows. Calcd.: Pb, 48.85%; ClO₄, 46.90%. Found: Pb, 48.85, 48.85; ClO₄, 47.06 (nitron), 46.67 (acid titration). A test of the methods of determining perchlorate (described on page 20) showed that the nitron method, using twice the theoretical amount of reagent, was excellent and that no correction for solubility loss was necessary if the prepipitate was transferred by means of the filtrate and washed with 10 cc. of ice water, added in 1–2 cc. portions, using slight suction. The removal of lead electrolytically tended to give slightly low results, perhaps due to slight loss by spraying. Precipitation of the lead by means of hydrogen sulfide and removal of the latter by boiling gave good results. No matter what method is used, the determination of perchlorate is less accurate than that of lead.

The melting point of Pb(ClO₄)₂·H₂O was found to be 153–155°. The above data prove the existence of this hydrate, which has not previously been obtained, and indicate that there is no lower hydrate.

Preparation of Lead Perchlorate Trihydrate.—A sample of lead perchlorate which had just been recrystallized was used. It contained 12.10% water as compared with 11.74% for the trihydrate. It was placed in a vacuum desiccator over a large excess of the monohydrate and the desiccator evacuated. It was allowed to stand for twelve months and then analyzed. Calcd.: Pb, 45.03; ClO₄, 43.73. Found: Pb, 45.17, 45.15; ClO₄ (nitron), 43.55, (acid titration), 43.20. The melting point of the trihydrate was 83–84°. The above data show the existence of the trihydrate and that another hydrate does not exist between the tri- and monohydrate.

Preparation of Basic Lead Perchlorate, Pb₃(OH)₄(ClO₄)₂.—This salt was prepared by saturating a hot solution of perchloric acid with lead oxide. The excess lead oxide was filtered out of the hot solution using a hot water funnel. On cooling, the basic salt crystallized in large irregular crystals. It was centrifuged in platinum cups and washed twice on the centrifuge with hot water. The salt was then crystallized from carbon dioxide-free water, centrifuged and washed. Weinland and Stroh⁷ state that this salt may be prepared by treating three moles of lead oxide with two moles of perchloric acid. When attempting to prepare other basic lead salts than those described by Weinland, it was discovered that this same salt could also be prepared by using lead oxide and perchloric acid in the molecular ratio of four to three. When the ratio of lead oxide to perchloric acid was less than 4 to 3 and greater than 2 to 3, a mixture of

¹¹ Storm, U. S. Bur. of Mines, Bull. 96, 1916, p. 65.

the above basic salt and another, described later, was obtained. This shows that the limits of the ratio for this basic salt are between 4 of oxide to 3 of acid and the saturation point of hot perchloric acid with lead oxide. The results of analysis are as follows. Calcd.: Pb, 69.96; ClO_4 , 22.39; OH, 7.65. Found: Pb, 70.05, 70.00; ClO_4 , 22.38, 22.36; OH, 7.65, 7.60.

The direct determination of hydroxyl was carried out as follows. The salt was dissolved in a slight excess of $N/10$ nitric acid. The solution was diluted and the lead precipitated as lead sulfate by adding excess of neutral sodium sulfate. After warming for a time it was cooled in ice and filtered. The excess acid was titrated with $N/10$ sodium hydroxide using phenolphthalein as indicator. It was observed that if the salt was dissolved in water, a turbidity appeared, probably due to a trace of carbonate, and if $N/10$ nitric acid was added slowly to the hot solution, the disappearance of the turbidity could almost be used as the end-point of the titration. It disappeared a trifle too soon, the difference being about 0.07 cc. of $N/10$ acid. Neither Marignac nor Weinland reported a determination of the hydroxyl group.

Preparation of $\text{Pb}_2(\text{OH})_2(\text{ClO}_4)_2 \cdot 1.5\text{H}_2\text{O}$.—Weinland and Stroh⁷ state that this salt may be prepared from a solution of lead oxide in the calculated quantity of perchloric acid. An attempt was made to prepare this salt by his method, and also by varying the ratio of lead oxide to perchloric acid. Although the analysis indicated the existence of a salt of the above composition, it was not conclusive. The variation in the results seemed to indicate a mixture rather than a salt of definite composition.

The Solubility of Lead Perchlorate.—A slight excess of lead perchlorate trihydrate was added to water in a glass tube, which was sealed up and rotated for several days in a thermostat at $25 \pm 0.005^\circ$. After settling for several days, some of the clear liquid was transferred to a pycnometer with a carefully ground stopper consisting of a tube with a capillary bore. The capacity of the pycnometer at 25° was found to be 9.9783 g. of water, or 10.0180 cc. The weight of lead perchlorate solution required to fill it was 27.7950 g., or 27.8029 g. corrected to vacuum. The calculated density is 2.7753. The solution was transferred to a beaker, precipitated as lead sulfate, filtered and weighed on a Gooch crucible after heating at 600° . The corrected weight of PbSO_4 was 16.9111 g., equivalent to 22.6464 g. of $\text{Pb}(\text{ClO}_4)_2$ or 25.6603 g. of $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$. The following table shows the solubility calculated from these figures.

TABLE I
SOLUBILITY OF LEAD PERCHLORATE IN WATER AT 25°
Density, $25^\circ/4^\circ$, 2.7753

	G. per 100 cc. of soln.	G. per 100 g. of soln.	Mole per 100 cc. of soln.	Mole per 100 g. of soln.
$\text{Pb}(\text{ClO}_4)_2$	226.103	81.472	0.55676	0.20061
$\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$	256.200	92.315		

Thiel and Stoll¹² called attention to the high density of the saturated solution and suggested its use as a heavy liquid for determining the specific gravity of organic substances. They stated that a solution saturated at 15° had a density of about 2.6 and contained 78% of lead perchlorate.

Anhydrous lead perchlorate is readily soluble in many organic solvents but work along this line was discontinued after the violent explosion of an almost saturated solution of this salt in anhydrous methyl alcohol. This solution was prepared by adding the perchlorate in small amounts to the

¹² Thiel and Stoll, *Ber.*, 53, 2003 (1920).

alcohol, cooling after each addition because considerable heat was given off during this process. The solution was cooled in ice to see if crystals would form. This did not occur, and the solution was allowed to warm up to room temperature. A little more of the salt was added and when the flask was disturbed the contents exploded.

Summary

1. Anhydrous lead perchlorate, the mono- and trihydrates, have been prepared in a high degree of purity and their properties studied.
2. One basic lead perchlorate, $\text{Pb}_3(\text{OH})_4(\text{ClO}_4)_2$, was prepared.
3. A method of determining the hydroxyl group in the basic salt is described.
4. The solubility of lead perchlorate in water at 25° is 81.472 g. per 100 g. of solution and the density is 2.7753.
5. A solution of anhydrous lead perchlorate in anhydrous methyl alcohol is explosive.

PART II

SOLUBILITIES

Introduction

It has been shown by Thiel and Stoll¹ that the difference in potential between lead electrodes in 0.05 molar solutions of lead perchlorate and nitrate is 0.016 volt. From this they calculated the ratio of the concentrations of Pb^{++} in the two solutions to be 1:0.28. In connection with other work it had been noticed that lead sulfate, chromate and molybdate were less soluble in perchloric acid than in nitric acid of the same concentration. In order to investigate this matter more thoroughly, with the possibility of utilizing the results in analytical separations, the solubilities of these salts were determined in perchloric and in nitric acids of different concentrations, both with and without the addition of a common ion.

Experimental

Preparation of Lead Sulfate.—Lead sulfate was prepared by adding simultaneously from two burets dilute solutions of sulfuric acid and lead perchlorate to 800 cc. of slightly acidified water, with vigorous stirring. This gave a fairly coarse precipitate. It was washed with water five times by decantation, centrifuged in platinum cups and washed four times on the centrifuge.

Preparation of Lead Chromate.—Lead chromate was prepared in the same manner as lead sulfate, using lead perchlorate and potassium dichromate. The lead chromate was washed with water eight times by decantation, four times on the centrifuge, dried in a vacuum over phosphorus pentoxide and analyzed by electrometric titration with ferrous sulfate. The average of two closely agreeing analyses gave 16.09% chromium, compared to a theoretical value of 16.08%.

Preparation of Lead Molybdate.—Lead molybdate was prepared in a similar manner by adding lead perchlorate and ammonium molybdate to hot water acidified with perchloric acid. After boiling the solution for a few minutes, the precipitate was washed eight times by decantation with hot 2% ammonium nitrate solution, centrifuged, and washed eight times on the centrifuge. Since it has been pointed out by Weiser² that lead molybdate occludes ammonium molybdate, the salt was further purified by stirring about 10 g. in a liter of normal perchloric acid for twenty-four hours. After it had settled, a 500-cc. sample of the clear solution was analyzed for lead and molybdenum and found to contain an excess of the latter, which must have been occluded as ammonium molybdate and subsequently extracted by the acid. The lead molybdate which had been stirred in perchloric acid was centrifuged and washed with hot 2% ammonium nitrate. After ignition it was analyzed, lead and molybdenum being separated by the sulfide method.³

¹ Thiel and Stoll, *Z. anorg. allgem. Chem.*, **139**, 317 (1924).

² Weiser, *J. Phys. Chem.*, **20**, 640 (1916).

³ Treadwell-Hall, "Quantitative Analysis," 7th ed., Vol. II, John Wiley and Sons, Inc., New York, 1928, p. 266.

Anal. Calcd.: PbO, 60.78. Found: 60.72, 60.76, 60.69, average, 60.72. Calcd.: MoO₃, 39.22. Found: 39.18, 39.14, 39.11, average, 39.14.

The lead molybdate possessed a yellowish-white tinge. This was also observed by Weiser.²

Preparation of Nitric and Perchloric Acids.—c. p. perchloric and nitric acids were redistilled in a vacuum. The different concentrations were made up from these by means of a hydrometer, using for perchloric acid the table by van Emster⁴ and for nitric acid the densities given by Lunge and Ray.⁵ The hydrometers were calibrated to read directly to 0.0005 at 15.5° and it was possible to estimate to 0.0001. The accuracy of this method of making up the acid concentrations was checked by titrating with standard alkali. The maximum error was about 0.002 *M* for higher concentrations and much less than this for the very dilute solutions.

Solubility Determinations.—Lead sulfate, lead chromate and lead molybdate were each placed in liter flasks and rotated with known concentrations of nitric and perchloric acids, respectively, in a thermostat which was not observed to vary as much as 0.001°. The water used in the acid solutions was twice distilled, using a block tin condenser and a quartz receiver. The flasks were closed with well ground stoppers covered with sheet rubber to keep the water in the thermostat from contact with the ground-glass joint. They were rotated for fifteen hours, then supported in a vertical position for two hours and the salt allowed to settle. Although the supernatant liquid was clear, the solutions were filtered through a platinum sponge filtering crucible into which they were siphoned directly from the flasks, the first portion being discarded. In this way it was possible to obtain samples absolutely free from particles of salt. A 500-cc. sample was taken for the low solubilities, and a 250- or 100-cc. sample for some of the higher ones. The results shown are the average of closely agreeing duplicates.

Solubility of Lead Sulfate in Perchloric and Nitric Acids.—Saturation of the solutions was carried out in quartz flasks with ground stoppers. After rotating lead sulfate in the thermostat as described, a 500-cc. sample was measured out, 1 cc. of concentrated sulfuric acid added and the solution concentrated in a quartz evaporating dish to about 25 cc. It was then transferred to a tared crucible, evaporated to dryness by means of a ring burner, and ignited at low red heat. It was possible to reproduce the weight of the crucible to within 0.05 mg. when the tare was ignited and cooled in the same way as the sample before each weighing. If the tare was not ignited each time, the variation was 0.1 mg. or more.

Solubility of Lead Sulfate Using a Common Ion.—The procedure was essentially the same except that the solutions were made up carefully from standard solutions so that when they were mixed and diluted to the re-

⁴ Van Emster, *Z. anorg. Chem.*, **52**, 270 (1907).

⁵ Lunge and Ray, *Z. angew. Chem.*, **4**, 165 (1891).

quired amount, the normalities would be as indicated in the tables. All the samples in which sulfuric acid furnished the common ion were analyzed by direct evaporation as explained above, except in a few cases in which the solubility was so low that lead was determined colorimetrically as sulfide.⁶

As there were no interfering substances present, the procedure was much simplified. A 500-cc. sample of the clear supernatant liquid was evaporated on the hot-plate and fumed until all the sulfuric acid was removed. The residue of lead sulfate was dissolved in ammonium acetate solution and diluted until the concentration of lead ion was low enough to determine colorimetrically, as determined by a preliminary test. Of this diluted solution, 25, 50 or 100 cc. (depending on the amount of lead present) was made ammoniacal with 5 cc. excess of concentrated ammonia water and diluted to a definite volume, as 100 cc. Lead sulfide was precipitated by adding 4 or 5 drops of the sodium sulfide solution. A standard was prepared in the same way and its color compared with that of the unknown. A blank was run in each case on the unknown before adding sodium sulfide. It was possible to check results within 5%.

In the solubilities in which lead perchlorate and lead nitrate furnished the common ion, it was necessary to determine the sulfate ion. This was done by removing most of the lead electrolytically from the original solution, concentrating the sample to about 75 cc. and removing the remaining lead. The solution was partially neutralized with sodium carbonate, after which the sulfate was precipitated with barium chloride. The weight of lead sulfate was calculated from the weight of barium sulfate obtained. The results are shown in Tables I and II.

It is interesting to note that the solubility of lead sulfate in perchloric acid increases up to a 2.0 *M* solution of acid and then decreases again, while the solubility of lead sulfate in nitric acid continues to increase with increasing acid concentration. Lead sulfate is much less soluble in perchloric acid than in nitric acid of the same concentration.

Solubility of Lead Chromate.—Saturation of the solutions with lead chromate was carried out in glass flasks with ground stoppers. The amount of lead chromate dissolved in the various concentrations of perchloric acid was determined by adding potassium iodide and titrating the iodine liberated with sodium thiosulfate using starch as indicator. For those in nitric acid the lead chromate was titrated electrometrically with 0.1 or 0.01 *N* ferrous sulfate. The solutions were concentrated to 150–200 cc., with addition of sulfuric acid when necessary, and cooled in ice before titrating. When lead perchlorate and lead nitrate furnished the common ion, the chromate was determined by electrometric titration with

⁶ Scott, "Standard Methods of Chemical Analysis," 4th ed., D. Van Nostrand Co., New York, 1925, p. 281.

TABLE I
SOLUBILITY OF LEAD SULFATE IN PERCHLORIC ACID AT 25°

Composition of solvent	PbSO ₄ dissolved in 100 cc. G.	Millimole
0.1 M HClO ₄	0.0278	0.0917
0.1 M HClO ₄ + 0.005 M H ₂ SO ₄	.0070	.0230
0.1 M HClO ₄ + 0.02 M H ₂ SO ₄	.0024	.0079
0.1 M HClO ₄ + 0.05 M H ₂ SO ₄	.0013	.0043
0.1 M HClO ₄ + 0.10 M H ₂ SO ₄	.0010 ^a	.0033
0.1 M HClO ₄ + 0.25 M H ₂ SO ₄	.0008 ^a	.0026
0.1 M HClO ₄ + 0.50 M H ₂ SO ₄	.0003 ^a	.0010
0.1 M HClO ₄ + 0.50 M Pb(ClO ₄) ₂	.0002	.0007
0.5 M HClO ₄	.0528	.1742
0.5 M HClO ₄ + 0.005 M H ₂ SO ₄	.0206	.0679
0.5 M HClO ₄ + 0.01 M H ₂ SO ₄	.0137	.0451
0.5 M HClO ₄ + 0.02 M H ₂ SO ₄	.0067	.0220
0.5 M HClO ₄ + 0.05 M H ₂ SO ₄	.0030	.0099
1.0 M HClO ₄	.0714	.2301
1.0 M HClO ₄ + 0.005 M H ₂ SO ₄	.0367	.1211
2.0 M HClO ₄	.0787	.2596
3.0 M HClO ₄	.0687	.2266
4.2 M HClO ₄	.0490	.1616

^a Lead determined colorimetrically.

TABLE II
SOLUBILITY OF LEAD SULFATE IN NITRIC ACID AT 25°

Composition of solvent	PbSO ₄ dissolved in 100 cc. G.	Millimole
0.1 M HNO ₃	0.0426	0.1405
0.1 M HNO ₃ + 0.005 M H ₂ SO ₄	.0078	.0257
0.1 M HNO ₃ + 0.05 M H ₂ SO ₄	.0015	.0049
0.1 M HNO ₃ + 0.25 M H ₂ SO ₄	.0011	.0036
0.1 M HNO ₃ + 0.50 M H ₂ SO ₄	.0009	.0030
0.1 M HNO ₃ + 0.50 M Pb(NO ₃) ₂	.0008	.0026
0.5 M HNO ₃	.0992	.3272
0.5 M HNO ₃ + 0.005 M H ₂ SO ₄	.0398	.1313
0.5 M HNO ₃ + 0.01 M H ₂ SO ₄	.0328	.1082
0.5 M HNO ₃ + 0.02 M H ₂ SO ₄	.0159	.0524
0.5 M HNO ₃ + 0.05 M H ₂ SO ₄	.0089	.0293
1.0 M HNO ₃	.2021	.6667
1.0 M HNO ₃ + 0.005 M H ₂ SO ₄	.1007	.3322
2.0 M HNO ₃	.3605	1.1890
3.0 M HNO ₃	.5389	1.7770
4.2 M HNO ₃	.7263	2.3960

ferrous sulfate. When sodium dichromate was used, the solution was analyzed for lead by reducing the dichromate with hydroxylamine hydrochloride, adjusting the acidity of the solution, and precipitating the lead with hydrogen sulfide. The lead sulfide was filtered, washed and dissolved in dilute nitric acid. This solution was boiled, neutralized and diluted to a suitable definite volume. Lead was then determined colori-

TABLE III

SOLUBILITY OF LEAD CHROMATE IN PERCHLORIC ACID AT 25°

Composition of solvent	PbCrO ₄ dissolved in 100 cc.	
	G.	Millimole
0.1 M HClO ₄	0.0041	0.0127
0.1 M HClO ₄ + 0.005 M Pb(ClO ₄) ₂	.0000	.0000
0.5 M HClO ₄	.0120	.0371
0.5 M HClO ₄ + 0.005 M Pb(ClO ₄) ₂	.0005	.0015
0.5 M HClO ₄ + 0.01 M Pb(ClO ₄) ₂	.0000	.0000
1.0 M HClO ₄	.0140	.0433
1.0 M HClO ₄ + 0.005 M Pb(ClO ₄) ₂	.0013	.0040
1.0 M HClO ₄ + 0.01 M Pb(ClO ₄) ₂	.0000	.0000
2.0 M HClO ₄	.0199	.0616
2.0 M HClO ₄ + 0.01 M Pb(ClO ₄) ₂	.0012	.0037
2.0 M HClO ₄ + 0.015 M Pb(ClO ₄) ₂	.0006	.0019
3.0 M HClO ₄	.0211	.0668
4.0 M HClO ₄	.0213	.0659
5.0 M HClO ₄	.0191	.0591
5.0 M HClO ₄ + 0.02 M Pb(ClO ₄) ₂	.0001	.0003
5.0 M HClO ₄ + 0.03 M Na ₂ Cr ₂ O ₇	.0000	.0000

TABLE IV

SOLUBILITY OF LEAD CHROMATE IN NITRIC ACID AT 25°

Composition of solvent	PbCrO ₄ dissolved in 100 cc.	
	G.	Millimole
0.1 M HNO ₃	0.0063	0.0195
0.1 M HNO ₃ + 0.005 M Pb(NO ₃) ₂	.0001	.0003
0.1 M HNO ₃ + 0.01 M Pb(NO ₃) ₂	.0000	.0000
0.5 M HNO ₃	.0177	.0548
0.5 M HNO ₃ + 0.005 M Pb(NO ₃) ₂	.0018	.0055
0.5 M HNO ₃ + 0.01 M Pb(NO ₃) ₂	.0000	.0000
1.0 M HNO ₃	.0385	.1190
1.0 M HNO ₃ + 0.01 M Pb(NO ₃) ₂	.0038	.0117
2.0 M HNO ₃	.0889	.2752
2.0 M HNO ₃ + 0.15 M Pb(NO ₃) ₂	.0012	.0037
2.0 M HNO ₃ + 0.25 M Pb(NO ₃) ₂	.0002	.0006
2.0 M HNO ₃ + 0.30 M Na ₂ Cr ₂ O ₇	.0002	.0006
3.0 M HNO ₃	.1701	.5265
3.0 M HNO ₃ + 0.02 M Pb(NO ₃) ₂	.0381	.1179
4.0 M HNO ₃	.2812	.8700
5.0 M HNO ₃	.4367	1.3510

metrically as described above. The results are shown in Tables III and IV.

In the case of lead chromate the solubility in perchloric acid increases up to 4.0 *M* acid and then begins to decrease, while the solubility in nitric acid continues to increase with increasing concentration of acid. Lead chromate is much less soluble in perchloric acid than in nitric acid of the same concentration.

Solubility of Lead Molybdate.—The solubility determinations of lead molybdate were carried out like those for lead chromate, and the supernatant liquid analyzed for both lead and molybdenum. This was done

by adding 4–6 cc. of concentrated sulfuric acid and evaporating to remove the perchloric acid or nitric acid. The solution was diluted, the lead sulfate filtered off, washed with 0.5% sulfuric acid, ignited and weighed. If molybdenum is carried down it is detected by a bluish tinge around the edge of the precipitate during ignition. After adjusting the acidity of the filtrate, the molybdenum was reduced to a trivalent salt by passing it through a Jones reductor, received in a ferric alum and phosphoric acid solution and titrated with permanganate.⁷ Perchloric acid must be absent because it oxidizes trivalent molybdenum even in dilute solution. The solubilities were discontinued at 1 *M* nitric and 3 *M* perchloric acid, because the molybdate seemed to be decomposed by the more concentrated acids, forming MoO_3 .

Two methods were used for determining the solubilities of lead molybdate when lead perchlorate and lead nitrate furnished the common ion. First, when the concentration of the salt giving the common ion was not greater than 0.05 *M*, the procedure was the same as that above, except that the

TABLE V
SOLUBILITY OF LEAD MOLYBDATE IN PERCHLORIC ACID AT 25°

Composition of solvent	PbMoO ₄ in 100 cc.	
	G.	Millimole
0.10 M HClO ₄	0.0016	0.0043
0.10 M HClO ₄ + 0.01 M Pb(ClO ₄) ₂	.0002	.0005
0.50 M HClO ₄	.0136	.0370
0.50 M HClO ₄ + 0.01 M Pb(ClO ₄) ₂	.0005	.0013
0.50 M HClO ₄ + 0.02 M Pb(ClO ₄) ₂	.0004	.0011
0.50 M HClO ₄ + 0.10 M Pb(ClO ₄) ₂	.00006 ^a	.0001
0.50 M HClO ₄ + 0.20 M Pb(ClO ₄) ₂	.00004 ^a	.0001
0.50 M HClO ₄ + 0.02 M Na ₂ MoO ₄	.0004 ^b	.0011
0.50 M HClO ₄ + 0.05 M Na ₂ MoO ₄	.00027 ^b	.0007
1.0 M HClO ₄	.0373	.1016
2.0 M HClO ₄	.1176	.3204
3.0 M HClO ₄	.2436	.6639

^a Mo determined colorimetrically. ^b Pb determined colorimetrically.

TABLE VI
SOLUBILITY OF LEAD MOLYBDATE IN NITRIC ACID AT 25°

Composition of solvent	PbMoO ₄ dissolved in 100 cc.	
	G.	Millimole
0.10 M HNO ₃	0.0020	0.0060
0.50 M HNO ₃	.0244	.0665
0.50 M HNO ₃ + 0.10 M Pb(NO ₃) ₂	.00032 ^a	.0009
0.50 M HNO ₃ + 0.20 M Pb(NO ₃) ₂	.0002 ^a	.0005
0.50 M HNO ₃ + 0.02 M Na ₂ MoO ₄	.00064 ^b	.0017
0.50 M HNO ₃ + 0.50 M Na ₂ MoO ₄	.0007 ^b	.0019
1.0 M HNO ₃	.1086	.2958

^a Mo determined colorimetrically. ^b Pb determined colorimetrically.

⁷ Ref. 6, p. 319.

supernatant liquid was analyzed only for molybdenum. With lower solubilities, where greater accuracy was required, the colorimetric method of King⁸ was used, with certain modifications. A 500-cc. sample was prepared by evaporating to fumes with a slight excess of sulfuric acid. The lead sulfate was filtered off and the molybdenum determined colorimetrically. Fifty cc. of the solution containing 2–3 cc. of concd. hydrochloric acid, about 2 cc. of concd. sulfuric acid and 1.5 g. of potassium thiocyanate was placed in a separatory funnel with the ether and cooled to 0°; 1 cc. of stannous chloride solution was added and the mixture shaken immediately. Two ether extractions were made, using 70 and 30 cc., respectively, but no color was obtained in the second.

When sodium molybdate furnished the common ion, the lead was separated by a double precipitation with alkaline sulfide,³ converted into sulfate, dissolved in ammonium acetate to free it from silica, and determined colorimetrically.⁶

The results are shown in Tables V and VI.

Lead molybdate, like the sulfate and chromate, is much less soluble in perchloric acid than in nitric acid of the same concentration. The solubilities could not be carried far enough to determine whether it would pass through a maximum in perchloric acid as with lead sulfate and chromate.

The solubilities suggest a number of quantitative separations, some of which were tested. The results of the latter, though preliminary in nature, are given.

Summary

1. The solubilities of lead sulfate, chromate and molybdate have been determined in perchloric and nitric acids, both with and without the addition of a common ion.

2. All these salts are much less soluble in perchloric acid than in nitric acid of the same concentration.

3. Both the sulfate and chromate pass through a maximum solubility in perchloric acid, and then, as the concentration of acid increases, the solubility decreases.

⁸ King, *Ind. Eng. Chem.*, **15**, 350 (1923).

PART III. ANALYTICAL ANALYTICAL METHODS

Determination of the Perchlorate Radical

Introduction.—Several methods have been described for determining the per cent. of ClO_4 in perchlorates. The method most generally adopted has been the decomposition of the perchlorate to chloride by fusion with sodium carbonate or sodium nitrite.¹ Lamb and Marden² fused the salt with sodium carbonate in a hard glass test-tube and used two asbestos plugs to prevent loss of the chloride by volatilization. They precipitated the chloride as silver chloride and obtained very good results. Dietrich and Ballenbach³ used a mixture of potassium nitrite and nitrate for reducing the perchlorate to chloride. Storm⁴ used nitron(1:4-diphenyl-3:5-indo-anilo-4:5-dihydro-1:2:4-triazole) to analyze two samples of ammonium perchlorate for ClO_4 . Nitron gives a precipitate of nitron perchlorate. König⁵ reduced perchlorates to chloride by means of titanous sulfate in an acid solution and titrated the excess titanous salt with ferric alum using potassium thiocyanate as indicator.

Modification of Marignac's Method.—Twice recrystallized potassium perchlorate was used for this work. When the perchlorate was decomposed with potassium nitrite or sodium carbonate low results were obtained, even though two asbestos plugs were used in the upper part of the tube. It seemed that the difficulty was due to the rapid evolution of the gas. Calcium oxide was used and gave excellent results because the reaction was more easily controlled. The potassium perchlorate was mixed with 3 g. of CaO , placed in a hard glass test-tube, and then another gram of CaO added. The tube was closed with two asbestos plugs as described by Lamb and Marden, and the tube with contents heated at low red heat in an electric furnace. This method gave 71.73% ClO_4 , compared to a theoretical of 71.78% for potassium perchlorate. Unsatisfactory results were obtained in the analysis of lead perchlorate, probably due to the tendency of lead to form basic salts.

Determination of ClO_4 in Lead Perchlorate.—(a) *Removal of lead with hydrogen sulfide.* A 1- to 2-g. sample of lead perchlorate was dissolved in 75–100 cc. of water in an Erlenmeyer flask and the lead precipitated

¹ Weinland and Stroh, *Ber.*, **55**, 2222 (1922).

² Lamb and Marden, *J. Am. Chem. Soc.*, **34**, 812 (1912).

³ Dietrich and Ballenbach, *Ber.*, **38**, 751 (1905).

⁴ Storm, Bureau of Mines, *Bull.* **96**, 65 (1916).

⁵ König, *Z. anorg. Chem.*, **120**, 48 (1922).

with hydrogen sulfide. The lead sulfide was filtered off, washed with H_2S water until free from perchloric acid. The test for perchloric acid was made by boiling a portion of the wash water until no test could be obtained for H_2S and then adding methyl red to the cooled solution. The washing was continued until no trace of acid could be obtained. The filtrate was concentrated to about 50 cc., and titrated with $N/10$ NaOH using methyl red as indicator.

Since the lead perchlorate used in the above analysis was not anhydrous a third sample was analyzed for lead by precipitating as lead sulfate. From this result the per cent. of perchloric acid was calculated for the other samples, and used as the theoretical value. 99.99 and 100.12% were obtained based upon the value for lead. This method is very satisfactory for determining the per cent. of ClO_4 in lead perchlorate.

(b) *Removal of lead electrolytically.*—This method was tried on the tri- and mono-hydrates of lead perchlorate. The salt was dissolved in 75 cc. of water, electrolyzed and the resulting solution titrated with standard alkali. There was a tendency for metallic lead to deposit in spongy form. This method gave slightly low results, which was partly accounted for by the loss of acid by spraying during electrolysis, or a slight action on the glass during evaporation. 46.67% ClO_4 was found compared to a theoretical of 46.90% for the mono-hydrate. For the tri-hydrate 43.20% ClO_4 was found compared to a theoretical of 43.23%.

Methylene Blue as a Precipitant for Perchlorate.—The methylene blue (an amount equal to five times the weight of the sample to be analyzed) was dissolved in 20 cc. of hot water and filtered while hot. A 0.1–0.20 g. sample of potassium perchlorate was dissolved in 30 cc. of water and the filtered hot solution of methylene blue was added slowly to the hot solution of potassium perchlorate. Long silky, yellowish-brown, needle-like crystals separated out. The solution was allowed to stand for forty-five minutes, cooled to 0°C . in ice and filtered, using slight suction. The beaker was washed with the filtrate and the precipitate was washed with ice water, about 20 cc. added in 2-cc. portions. One hundred cc. of ice water dissolved 0.0022 g. of methylene blue perchlorate from a 0.2936-g. sample. This same sample, in ice cold 95% ethyl alcohol lost 0.0021 g. Analyses by this method gave 71.29 and 71.32% compared to a theoretical of 71.78%. If the right conditions for precipitation could be determined this method might be used.

Nitron as a Precipitant for Perchlorate.—The method as given by Storm for precipitating perchlorate with nitron was used and found very satisfactory. Storm used three times the theoretical amount of nitron but it was found that twice this amount was sufficient. When the precipitate was washed with 10 cc. of ice water, added in 1–2-cc. portions with slight suction, no correction was necessary for loss during washing.

Determination of Molybdenum Using the Jones Reductor

Scott⁶ in describing the titration of molybdenum after reduction in a Jones reductor, states that the KMnO_4 should be standardized against a standard molybdic acid solution. This was investigated by standardizing a solution of KMnO_4 in the usual manner against sodium oxalate and then against molybdic acid (Mallinckrodt), which had been ignited at about 400°C . for about four hours. The factors obtained with sodium oxalate were 0.10312 and 0.10310 *N* compared to 0.10307 and 0.10310 *N* with molybdic acid. The first drop of KMnO_4 gave a distinct color to a blank that had been passed through the Jones reductor. The above results are conclusive proof that the factor obtained with sodium oxalate is the same as that with molybdic acid.

Separation of Molybdenum from Iron and Chromium.—The two most general methods for the separation of molybdenum and iron in steel are: (1) precipitation of molybdenum as sulfide from slightly acid solution,⁶ and (2) precipitation of iron as ferric hydroxide by pouring the acid solution into hot sodium hydroxide solution.⁶ Weiser⁷ describes a method for the precipitation of molybdenum as lead molybdate from a dilute nitric acid solution. The last traces of lead molybdate are afterward removed by adding ammonium or sodium acetate. This method is not applicable to steel because iron would be carried down as the basic acetate. The method described by Weiser has the additional objection in that lead molybdate is somewhat soluble in an acetate solution.

Fenwick⁸ pointed out that molybdenum might be separated from chromium and vanadium as lead molybdate from a 2% perchloric acid solution, but when iron was present it was always adsorbed to some extent.

From the low solubility of lead molybdate in perchloric acid as given in Table V, it seemed that this might be made the basis of an analytical method. A very interesting and unexpected fact was discovered, that molybdenum could be separated from either chromium or iron satisfactorily, but when they were both present, a small amount of iron was always carried down by the precipitate.

Precipitation was carried out at about 100°C . The precipitate formed slowly and it was often necessary to keep the solution at the boiling point a few minutes before it appeared. If too much precipitant was added before the precipitate formed, the lead molybdate was rather fine and required about one-half hour to settle. The lead molybdate was filtered

⁶ Scott, "Standard Methods of Chemical Analysis," 4th ed., 1925, pp. 319, 317, 314. D. Van Nostrand Co., New York.

⁷ Weiser, *J. Phys. Chem.*, **20**, 640 (1916).

⁸ Florence Fenwick, "Dissertation," University of Michigan, 1922, p. 58.

on an asbestos filter and washed with $M/10$ perchloric acid $M/10$ in lead perchlorate. The final washing was made with 2% ammonium nitrate solution. The salt was then ignited at low red heat and weighed as lead molybdate.

DETERMINATION OF MOLYBDENUM IN THE PRESENCE OF CHROMIUM

Cr added as $\text{Cr}(\text{ClO}_4)_3$, g.	MoO_3 added, g.	Acidity, M	Final vol., cc.	Conc. of excess $\text{Pb}(\text{ClO}_4)_2$, M	MoO_3 found, g.
0.31	0.1334	0.25	70	0.1	0.1332
.52	.1210	.25	70	.1	.1208

No chromium was found in the lead molybdate but a slight trace of molybdenum was present in the filtrate.

DETERMINATION OF MOLYBDENUM IN THE PRESENCE OF IRON

Fe added as $\text{Fe}(\text{ClO}_4)_3$, g.	MoO_3 added, g.	Acidity, M	Final vol., cc.	Conc. of excess $\text{Pb}(\text{ClO}_4)_2$, M	MoO_3 found, g.
1.0	0.2180	0.25	75	0.1	0.2178
2.5	.1489	.25	100	.1	.1489

No trace of iron was found in the lead molybdate.

DETERMINATION OF MOLYBDENUM IN THE PRESENCE OF CHROMIUM AND IRON

Fe added as $\text{Fe}(\text{ClO}_4)_3$, g.	Cr added as $\text{Cr}(\text{ClO}_4)_3$, g.	MoO_3 added, g.	Acidity, M	Conc. of $\text{Pb}(\text{ClO}_4)_2$, M	MoO_3 found, g.	Fe present in ppt., mg.
1.5	0.31	0.1756	$1/3$	0.2	0.1748	0.5
1.5	.52	.1921	$1/3$	.2	.1912	.6

The final volume in each case was 100 cc. Other samples were analyzed but the above are typical examples.

Determination of the Lead Alloys

The alloy is dissolved in a mixture of nitric and hydrofluoric acids. The latter is added to keep tin and antimony in solution as complex fluoride. The acidity may then be adjusted in either of the following ways: (1) by neutralizing with ammonia and then adding 3 M nitric acid so that the acidity will not be over 0.1 M when the solution is diluted to about 200 cc.; (2) by partially neutralizing with ammonia and adding 5 g. of sodium acetate and 5 cc. of glacial acetic acid before diluting to 200 cc.

The lead is precipitated at the boiling point by the addition of either potassium or sodium dichromate, heated for a few minutes, cooled, filtered on an asbestos mat and washed with hot water. The lead chromate is dissolved in a hot solution of concentrated sodium chloride, containing a small amount of hydrochloric acid. It is reduced by adding an excess of standard sodium arsenite, more concentrated HCl , and then the excess of sodium arsenite titrated while hot with standard bromate, using methyl orange as indicator.

Bureau of Standards brass No. 37b, gave 0.881, 0.905, 0.884% Pb instead of 0.90%.

Tin base bearing metal No. 54 gave 0.553, 0.550, 0.572% Pb instead of 0.56%.

While this method has been applied successfully to a few alloys, further work is necessary to prove its validity in all cases.

Summary

1. The perchlorate radical in lead perchlorate is best determined by precipitation as nitron perchlorate, or by titration with alkali after removing the lead electrolytically or by hydrogen sulfide.

2. In the volumetric determination of molybdenum the theoretical factor for permanganate may be used.

3. Molybdenum may be separated from iron or from chromium but not from both, by precipitation as lead molybdate in perchloric acid solution.

4. Lead, in alloys with copper, tin and antimony may be determined volumetrically by precipitation as chromate in a slightly acid solution of hydrofluoric and nitric acids, and titration of the chromate by arsenite.

